# Novel Sulphonylating reagent: Sulphuric Acid–Hexafluoroacetic Anhydride

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*Summary* A mixture of sulphuric acid and hexafluoroacetic anhydride is an efficient reagent for the sulphonylation of aromatic compounds.

THE sulphonylating potential of the system arylsulphonic acid–hexafluoroacetic anhydride has been noted before.[1,2] More recently, sulphones have been synthesised using alkyl-[3] or aryl-sulphonyl trifluoromethanesulphonates,[4] which are first prepared from silver trifluoromethanesulphonate and the corresponding alkyl- or aryl-sulphonyl bromide. Sulphonylations using systems containing sulphuric acids have been examined in detail,[5] but the reported yields are low. We have succeeded in synthesising diaryl sulphones in high yields using simple reagents, namely sulphuric acid and hexafluoroacetic anhydride.

With acetic anhydride and its homologues, sulphuric acid gives[6–8] acylsulphuric acids and diacyl sulphates. The latter are acylating agents,[6] whereas acetylsulphuric acid behaves, depending on the conditions,[7,8] both as an acetylating and as a sulphonating agent. By analogy, our kinetic data show that sulphuric acid gives with hexafluoroacetic anhydride, depending on the conditions, either trifluoroacetylsulphuric acid or di-trifluoroacetyl sulphate.

The sulphonylating reagent was prepared by equilibrating (*ca.* 15 min) sulphuric acid (1 mol. equiv.) with hexafluoroacetic anhydride (2 mol. equiv.). Better yields were obtained if nitromethane was used as solvent. The sulphonylation occurred readily when the aromatic compound (2 mol. equiv.) was added at room temperature, and the temperature was raised merely to increase the yields slightly. With benzene as the aromatic compound the transformations may be represented as in equations (1) and (2). Sulphonylating behaviour has also been

$$H_2SO_4 + 2(CF_3CO)_2O \rightarrow (CF_3CO_2)_2SO_2 + 2\ CF_3CO_2H \qquad (1)$$

$$(CF_3CO_2)_2SO_2 + 2PhH \rightarrow PhSO_2{\cdot}Ph + 2\ CF_3CO_2H \qquad (2)$$

observed using methanesulphonic anhydride in place of hexafluoroacetic anhydride, and with anisole the yield of the diaryl sulphones was 80%.

Table. Preparation of diaryl sulphones

| | Diphenyl sulphone | | |
|---|---|---|---|
| Substrate | Overall yield/% | Substituents[a] | Mole fraction of isomer |
| PhH | 61 | — | — |
| PhMe | 88 | 4,4′-$Me_2$ | 0·62 |
| | | 2,4′-$Me_2$ | 0·36 |
| | | 3,4′-$Me_2$ | 0·02 |
| PhEt | 83 | 4,4′-$Et_2$ | 0·72 |
| | | 2,4′-$Et_2$ | 0·12 |
| | | 3,4′-$Et_2$ | 0·16 |
| $PhPr^i$ | 80 | 4,4′-$Pr^i_2$ | 0·80 |
| | | 2,4′-$Pr^i_2$ | 0·05 |
| | | 3,4′-$Pr^i_2$ | 0·15 |
| Mesitylene | 99 | 2,2′,4,4′,6,6′-$Me_6$ | 1 |
| *m*-Xylene | 73 | 2,2′,4,4′-$Me_4$ | 1 |
| PhOMe | 99 | 4,4′-$(MeO)_2$ | 0·62 |
| | | 2,4′-$(MeO)_2$ | 0·38 |
| PhOEt | 96 | 4,4′-$(EtO)_2$ | 0·62 |
| | | 2,4′-$(EtO)_2$ | 0·38 |
| $Ph_2CH_2$ | 75 | 4,4′-$(PhCH_2)_2$[b] | |
| PhCl | 36 | 4,4′-$Cl_2$[b] | |

[a] The main products were obtained in crystalline form Their m.p.s were in accordance with literature data, and they gave satisfactory $^1H$ n.m.r. and mass spectra. [b] Main product after crystallisation.

The reagent did not react significantly with nitrobenzene but nevertheless reacted with an arene as unreactive as chlorobenzene. Where isomeric diphenyl sulphones were expected the major isomer (*cf.* Table) comprised over 60% (g.l.c.) of the total product and the isomer distribution indicated regiospecificity in one of the two consecutive aromatic substitutions. Such a reaction course has been exploited in the synthesis of sulphones possessing two different aryl groups and will be described elsewhere.

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